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COMMENT

Comment on 'Extrinsic versus intrinsic ferroelectric switching: experimental investigations using ultra-thin PVDF Langmuir–Blodgett films'

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Abstract
Previous work on ultra-thin P(VDF-TrFE) Langmuir–Blodgett films has indicated a transition from extrinsic to intrinsic ferroelectric switching. The lack of several key features of intrinsic switching in the experimental work reported by Kliem *et al* argues against intrinsic switching. In this Comment we discuss two published papers and new experimental results that support a lack of intrinsic switching and point to the conclusion that the thickness dependence of the Langmuir–Blodgett films is due to the influence of the electrode interfaces.

Kliem *et al* [1] have recently made an interesting contribution on the ferroelectric switching of ultra-thin Langmuir–Blodgett (LB) films of ferroelectric polymer poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) in metal–ferroelectric–metal capacitors. The question that was addressed was whether the ferroelectric switching behaviour in these films is 'extrinsic' (with nucleation-growth switching relaxation) or 'intrinsic' (with suppressed nucleation). Several new and important experimental results were obtained that favour extrinsic switching and argue against intrinsic switching. In this Comment, we briefly review all the papers on the subject to place [1] in a broader scope and to establish the main question: what is the physical reason for the thickness dependence of the ferroelectric behaviour of the LB films? We then summarize two published papers which showed that the influence of the capacitor electrodes is a better explanation for the thickness dependence than intrinsic switching. This alternative explanation supports the findings in [1]. Here we present additional measurements that confirm the influence of the capacitor electrodes.

In 2000 a pioneering work on capacitors with ultra-thin LB films of P(VDF-TrFE) and aluminium electrodes demonstrated the film thickness dependence of the coercive field E_c for thicknesses between 100 and 1 nm [2]. With decreasing thickness, E_c first increases and then saturates below a thickness of 15 nm, to a value of 5 MV cm^{-1}. This increase and saturation of E_c was explained by a transition from extrinsic to intrinsic ferroelectric switching in the context of Landau–Ginzburg mean-field theory. Several scientific groups questioned the intrinsic nature of the switching [3–7]. A follow-up report on [2] about the same LB films showed that they switch a million times slower than the bulk material, which was argued to be consistent with the intrinsic switching dynamics derived from the Langrange equation for the Gibbs free energy [8]. It was also reported that the films do not switch at all below the coercive field. This was explained by a generic property of intrinsic switching, namely, that the dipoles are highly correlated and therefore switch either coherently or not at all. Reports [2] and [8] therefore point to the conclusion that the experimentally observed thickness dependence of the LB films is explained by intrinsic switching. However, the experiments described in [1] can be summarized as follows.

(i) The coercive field does not saturate with decreasing film thickness.

(ii) The switching time dependence on the applied electric field and temperature are not well described by the intrinsic switching dynamics derived from the Langrange equation for the Gibbs free energy [8].
(iii) The films switch to some degree below the coercive field.

As discussed in [1], results (i) and (iii) argue against intrinsic switching while result (ii) can perhaps be addressed by modifying the theoretical model. But if intrinsic switching does not occur then why are the coercive field and the switching kinetics thickness dependent?

Several possible mechanisms have been proposed for an increase of E_c in ferroelectric thin film capacitors, including domain wall pinning [9], built-in depletion field-assisted switching [10] and nearby-electrode charge injection [11, 12]. The last two models do not apply to the LB films because P(VDF-TrFE) is not a semiconductor. Domain wall pinning appears to be an applicable explanation for the results reported in [1], but the model has not yet been applied to the LB films in a quantitative way. A mechanism that applies specifically to the LB films was proposed in 2003 [13]. The mechanism implies a small separation between the compensation charges and the electrode interfaces. The model could explain the experimentally observed thickness dependence of the coercive field of the LB films in a quantitative way without introducing intrinsic ferroelectric switching. We note that a previous theoretical discussion on a similar mechanism predicted a different coercive field thickness dependence due to the use of a different set of underlying assumptions [14]. This issue is the subject of an ongoing discussion. An alternative explanation for the thickness dependence of the switching kinetics was reported in 2004 [15]. An experimental work on spin coated P(VDF-TrFE) films with a thickness of down to 60 nm compared the use of conductive polymer and aluminium bottom electrodes. It was shown that the switching kinetics are dependent on the film thickness with aluminium electrodes but not with conductive polymer electrodes. The capacitors with LB films were made with aluminium electrodes [2, 8], so it is reasonable to conclude that the thickness dependence was induced by the use of aluminium. Reports [13] and [15] therefore indicate that the experimentally observed thickness dependence of the LB films is not a characteristic of P(VDF-TrFE) but a characteristic of the electrode interfaces. This alternative explanation for the thickness dependence of the LB films supports the lack of intrinsic switching reported in [1].

To emphasize the important role of the electrode interfaces, we investigated the thickness scaling of capacitors with gold electrodes. Previously, our attempts to make capacitors with noble metals most often resulted in making contact between the top and bottom contact, but we recently demonstrated how to solve this problem with an optimized spin coating technique [16]. With a few additional optimizations we could scale the thickness down to 60 nm to make the films directly comparable to 64 nm thick LB films [1]. The capacitors were prepared on clean glass substrates. For the bottom electrodes, a 1 nm thick chromium adhesion layer and a 15 nm thick gold layer were deposited by shadow mask evaporation, followed by an UV ozone treatment to remove any organic impurities [17]. Solutions of poly(vinylidene fluoride-trifluoroethylene) 65–35 mole% random copolymer (Solvay Duphar, Belgium) in cyclohexanone were prepared and filtered at 60 °C and spin coated at room temperature with a rotation speed of 4000 rpm. The film thickness was varied by concentration adjustment. During the spin coating procedures, the atmospheric humidity was controlled to less than 20% using a dry N_2 gas flow because a high humidity can affect the film morphology [18]. The films were annealed in a vacuum oven for 2 h at 138 °C with slow heating and cooling rates. Capacitors with a crossbar layout and an area of 1 mm^2 were completed by evaporation of 50 nm thick gold electrodes. Polymer film thicknesses were determined using a Dektak profilometer.

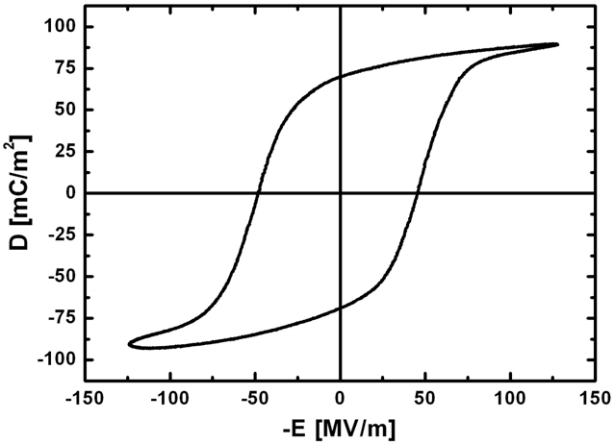

Figure 1. Charge displacement D versus applied electric field E of a ferroelectric capacitor with gold electrodes and a ferroelectric polymer film thickness of 60 nm. The measurement was performed with a Sawyer–Tower circuit at a frequency of 100 Hz.

In figure 1 the charge displacement D versus applied field E measurement of a capacitor with gold electrodes and a ferroelectric polymer film thickness d of 60 nm is presented. Identical charge displacement curves were measured for $d =$ 80, 100, 130 and 155 nm. The derived values for the coercive field $E_c = 47\,\mathrm{MV\,m^{-1}}$, the remanent polarization $P_r = 70\,\mathrm{mC\,m^{-2}}$ and the switching frequency of 100 Hz are all normal values for the bulk material [19]. This shows that the ferroelectric properties of P(VDF-TrFE) films are thickness independent down to 60 nm. This is not the case with aluminium electrodes, as evidenced by a switching frequency decrease to 1 mHz and an E_c increase [1]. The E_c increase is presented in figure 2. For a d value of 60 nm, E_c is either $150\,\mathrm{MV\,m^{-1}}$ with aluminium electrodes or $47\,\mathrm{MV\,m^{-1}}$ with gold electrodes. This means that aluminium induces a threefold increase of E_c and a 10^5-fold decrease in the switching frequency when $d = 60$ nm. This strengthens the conclusion that the thickness dependence of the LB films is not a characteristic of P(VDF-TrFE) but a characteristic of the electrode interfaces. We note that a very recent paper reports on ultra-thin P(VDF-TrFE) film capacitors with gold electrodes and diethyl carbonate as the spin coating solvent [20]. A comparison of the results with aluminium electrodes showed that the gold electrodes enhance the thickness scaling of the remanent polarization and the switching kinetics, which confirms the results presented in this Comment. The

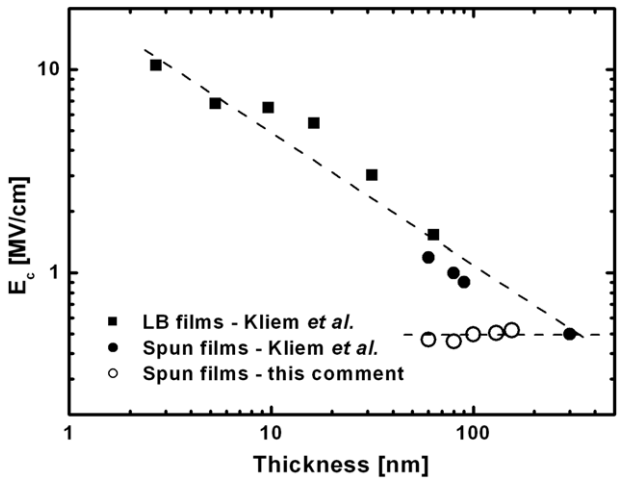

Figure 2. Coercive field E_c versus the film thickness of ferroelectric polymer P(VDF-TrFE). The filled symbols were extracted from figure 7 in [1]. The open symbols are results on ferroelectric capacitors with gold electrodes.

paper does not address the thickness scaling of the coercive field.

In summary, pioneering work on ultra-thin P(VDF-TrFE) Langmuir–Blodgett films indicated a transition from extrinsic to intrinsic ferroelectric switching [2, 8]. The lack of several key features of intrinsic switching in the experimental work reported in [1] argues against intrinsic switching. Two published papers [13, 15] and the results presented in this Comment support a lack of intrinsic switching and point to the conclusion that the thickness dependence of the LB films is due to the influence of the electrode interfaces. We hope that this understanding will invoke new theoretical and experimental work to address the problem of making contacts to ultra-thin P(VDF-TrFE) films without affecting its properties. We note that this experimental problem is similar to the electrode interface effects that occurred when making contact with other bistable molecules such as rotaxanes [21], which shows that this kind of problem is fundamental to science of molecular electronic devices.

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